An X-ray spectroscopic study of red-phosphor (Pr, Al)-doped SrTiO₃ fine particles

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Introduction

A red phosphor (Pr, Al)-doped SrTiO₃ fine particle has perovskite structure with 15% Ti in oxygen-octahedrons and 0.2% Sr at corner sites substituted by Al and Pr correspondingly. Under UV irradiation with photon energy higher than the band gap of ~3.2 eV, red brilliant light is emitted. This powder phosphor is already in practical use for display panels such as a vacuum fluorescent display [1]. Recently, the host crystal SrTiO₃ has attracted much interest of many researchers from a viewpoint of photoinduced phase transition: under UV irradiation, SrTiO₃ undergoes phase transition from a quantum paraelectric state to a ferroelectric one together with a faint green luminescence.

In this report, we present the X-ray absorption spectra (XAS) of (Pr, Al)-doped $SrTiO_3$ under UV irradiation, which is quite similar to that of a $SrTiO_3$ single crystal [2]. The analogous feature of photoabsorption and luminescence mechanism is briefly discussed.

Experimental

Three (Pr, Al)-doped $SrTiO_3$ fine particles were prepared. In this report, the result of a sample with highest luminous efficiency is presented. The powder sample is manufactured by a solid-phase method and its average particle size is $2\sim3\mu m$.

Ti K-edge XAS experiments were performed on BL-7C using a Si(111) double-crystal monochromator and a higher-order harmonic-rejection mirror. The spectra were measured using transmission technique at room temperature. A Hg-Xe lamp of 50mW/ cm² (Hamamatsu Photonics K.K., Lightningcure LC5) was used as a UV light source.

Results and Discussion

Figure 1 shows Ti *K*-edge XAS of (Pr, Al)-doped SrTiO₃ with (red dots) and without (black dots) UV irradiation. The spectra are normalized to unity at 4993 eV. In both spectra, three characteristic peaks (A_1 , A_2 and A_3) followed by main edge jumps are observed. The difference spectra is also shown in the figure (a blue line), showing two remarkable peaks labeled B_1 and B_2 . Surprisingly enough, a quite similar result is obtained for a SrTiO₃ single crystal in a quantum paraelectric state which indicates the almost same mechanism for photoabsorption and luminescence.



Figure 1. Normalized Ti *K*-edge X-ray absorption spectra with (red dots) and without (black dots) UV irradiation. The difference spectra is also shown by a blue line.

The causes of B_1 and B_2 peaks are completely different. Firstly, the B_1 peak corresponds to the A_2 peak in XAS, which is well assigned to a quadrupole transition from Ti 1s to $3d-e_s$ states. Under UV irradiation, the A_2 peak enhances its intensity that results in the single B_1 peak in the difference spectra. In the case of SrTiO₃ single crystal, the uniaxial vibration of the Ti atom along Ti-O direction under UV irradiation is already concluded, therefore the same vibronic motion could be expected for (Pr, Al)-doped SrTiO₃.

Secondly, the B_2 peak as well as the rest of other features in higher energy region is differential form of XAS. This is simple due to a chemical shift toward lower photon energy caused by UV irradiation. Two plausible causes can be proposed, a thermal lattice expansion and/or relatively longer lifetime of valence holes. We lack conclusive evidence which is more reliable, however, the fact that can be stressed is that the energy of UV light is absorbed by the vibration of Ti atoms and is transferred to, e.g., Pr or excitonic states, then resulting the luminescence of both (Pr, Al)-doped and a quantum paraelectric SrTiO₃.

References

- [1] H. Yamamoto, S. Okamoto, Displays 21, 93 (2000).
- [2] S. Nozawa, T. Iwazumi, and H. Osawa, Phys. Rev. B72, 121101(R) (2005).